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54 Title of the Invention: Method for the production of manganese oxide powder

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SPECIFICATION

1. Title of the Invention

Method for the production of manganese oxide powder

2. Claims

1. Method for the production of manganese oxide powder, characterized by heating the liquid drops afforded by spraying an aqueous solution of a manganese compound.

2. Method according to Claim 1 for the production of manganese oxide powder, in which a lithium compound is dissolved in the said aqueous manganese compound solution.

3. Detailed Description of the Invention

Field of the Invention

This invention relates to methods for the production of manganese oxide powder. More particularly, the present invention relates to a method for the preparation of a highly dispersible, highly packable spherical manganese oxide powder that can be used, for example, as the active substance in the positive electrode of lithium secondary batteries.

Description of the Prior Art and Problems to Be Solved by the Invention

Manganese oxide powder is at present generally produced by mechanically grinding electrolytic manganese oxide or amorphous manganese oxide afforded by oxidation of a manganese compound and classifying and collecting the grinding product.

Unfortunately, this method suffers from several problems. The process is complicated and the yield of collected manganese oxide is low. Moreover, the collected manganese oxide contains high levels of impurities. Finally, the product is amorphous in shape rather than spherical and as a result it has a low packability.

The poor packing behavior caused by the amorphous shape of ground and classified manganese oxide powder places limitations on its performance, for example, as the positive electrode material of lithium secondary batteries.

In addition, this type of manganese oxide powder suffers from high production co ts and. as stated above. it contains high levels of impurities.

With these circumstances as background, the object of the present invention is to provide a method for the production of a spherical, highly packable manganese oxide powder that does not suffer from any loss in quality or physical properties.

Means Solving the Problems

As a result of extensive investigations directed to achieving the aforesaid object, the inventors discovered that spraying an aqueous solution of a manganese compound with a sprayer and thermally decomposing the resulting liquid drops in air affords a spherical manganese oxide powder that has a much better dispersibility and packability than the manganese oxide provided by prior-art production methods. This invention was developed as a result of this discovery.

In specific terms, the present invention relates to a method for the production of spherical manganese oxide powder, wherein said method is characterized by heating the liquid drops afforded by spraying an aqueous solution of a manganese compound.

The preparative method according to the present invention will be explained below.

A manganese compound is used as the starting material by the present invention. This manganese compound will usually be manganese nitrate or manganese carbonate, but manganese sulfate or manganese chloride can also be used. The starting manganese compound is dissolved in pure water to prepare an aqueous solution of the manganese compound. The manganese concentration in this solution will preferably be about 50 to 400 g/L.

The present invention also includes the dissolution of a lithium compound, e.g.. lithium hydroxide, lithium carbonate, lithium nitrate, etc., in the aqueous manganese compound solution. In this case the preferred manganese concentration is about 50 to 300 g/L. This addition of a lithium compound provides a maximal facilitation of lithium ion diffusion in the manganese oxide.

The aqueous manganese compound solution thus prepared is then sprayed in the method according to the present invention using a sprayer in order to generate liquid drops. The sprayer used for this purpose is not critical, and a supersonic sprayer, for example, can be used.

These liquid drops are then heated in order to give spherical manganese dioxide or composite manganese/lithium oxide. Suitable heating conditions here are 150°C to 900°C and 1 to 5 minutes.

The heating apparatus depicted in Figure 1 is provided as one example of an apparatus that can be used to heat the liquid drops. In the figure. 1 refers to a supersonic humidifier, 2 refers to a reaction tube, 3 refers to an electric furnace, 4 refers to a temperature controller, 5 refers to a collector, 6 refers to water, and 7 refers to a suction fan.

Function

The function of the present invention remains incompletely understood, but the following mechanisms can be hypothesized.

① An excellent packing behavior is obtained due to the absence of sintering and because a spherical monodispersion is generated.

② A low impurity level is obtained due to the uniformity of the composition.

As a consequence of the synergistic effects of these mechanisms, the present invention produces a very pure spherical manganese oxide that exhibits an excellent packing behavior and an excellent dispersibility.

Examples

The invention will be specifically explained below through working and comparative examples.

Example 1

Manganese nitrate was dissolved in pure water to give an aqueous solution with a manganese concentration of 64.5 g/L. This aqueous solution was sprayed at a spray rate of 1 mL/minute and the resulting liquid drops were heated in the apparatus shown in Figure 1 at 500°C for 1 minute to give the spherical manganese oxide powder shown in the micrograph in Figure 2 (3,000x).

The physical values of this manganese oxide powder are reported in Table 1. Its particle sizes and packability are reported in Table 2.

The particle size distribution reported in Table 1 was measured using a Microtrack SPA particle size analyzer from Nikkiso. The smaller particle sizes were sieved out first. The particle sizes are reported immediately before reaching 10, 50, and 90 weight% of the total weight.

The packability, which is a factor that affects battery performance, was measured by the following methodology.

$$\text{packability} = \frac{\text{particle size } (\mu) \text{ by light transmission}}{\text{particle size } (\mu) \text{ by air permeation}}$$

The particle size by light transmission in this formula refers to the median particle size in the particle size distribution measured by light transmission using a centrifugal sedimentation particle size distribution analyzer from Shimadzu. The particle size by air permeation refers to the median particle size in the particle size distribution measured by air permeation using a model SS-100 (Shimadzu) specific surface area analyzer.

Example 2

Liquid drops prepared by the same method as in Example 1 were heated in a heater as shown in Figure 1 for 1 minute at 700°C to give the spherical manganese oxide powder shown in the micrograph in Figure 3 (3,000x).

The physical values of thi manganese oxide powder, which were obtained as in Example 1, are reported in Table 1. The particle

sizes and packability are reported in Table 2.

Example 3

An aqueous lithium hydroxide solution was added to a solution of manganese carbonate dissolved in excess nitric acid to give an aqueous solution with a manganese concentration of 64.5 g/L and a lithium concentration of 3.3 g/L. This aqueous solution was sprayed at a spray rate of 1 mL/minute and the resulting liquid drops were heated in the above-described apparatus for 1 minute at 500°C to give the spherical manganese oxide powder shown in the micrograph in Figure 4 (3,000x).

The physical values of this manganese oxide powder, which were obtained as in Example 1, are reported in Table 1. The particle sizes and packability are reported in Table 2.

Comparative Example 1

Electrolytic manganese dioxide prepared by an electrolytic method was mechanically ground and then classified to give manganese dioxide powder whose shape is shown in the micrograph in Figure 5 (3,000x).

The physical values of this manganese oxide powder, which were obtained as in Example 1, are reported in Table 1. The particle sizes and packability are reported in Table 2.

Table 1.[1]

Example, Comp. Example	sprayed solution	sprayed solution concen-tration g/L	heating temp. °C	particle size distribution µm < 10%	< 50%	< 90%	specific surface area m^2/g	analytic values % MnO_2	T-Mn	Li
Ex. 1	$Mn(NO_3)_2$	Mn = 64.5	500	0.98	2.53	5.61	103.5	52.73	57.46	—
Ex. 2	$Mn(NO_3)_2$	Mn = 64.5	700	0.90	2.26	4.47	68.1	44.94	57.30	—
Ex. 3	$Mn(NO_3)_2$ LiOH	Mn = 64.5 Li = 3.3	500	1.08	3.26	9.13	87.6	39.17	40.41	0.20

1 Translator's Note. I can confirm that Table 1 in the Japanese source document does not contain a row for Comparative Example 1.

Table 2.

Example, Comparative Example	median particle size by light transmission D_1 (μ)	median particle size by air permeation D_2 (μ)	packability D_1/D_2
Example 1	1.45	0.45	3.22
Example 2	1.90	0.66	2.88
Example 3	1.56	0.55	2.84
Comparative Ex. 1	1.26	0.91	1.38

As demonstrated in Tables 1 and 2, the manganese oxide powders in Examples 1 to 3 have small particle size distributions and also have higher packabilities than in Comparative Example 1.

As shown in Figures 2 to 5, the manganese oxide powder prepared in Comparative Example 1 has an amorphous shape while the manganese oxide powders of Examples 1 to 3 are spherical.

These results confirm that the manganese oxide powders of Examples 1 to 3 have an excellent packability and dispersibility.

Effects of the Invention

As the preceding explanation has made clear, the manganese oxide powder provided by the production method according to the present invention is spherical, has an excellent packing behavior, and has an excellent dispersibility. In consequence thereof it can be used in a wide range of applications, for example, as the active material in the positive electrode of lithium secondary batteries.

4. Brief Description of the Figures

Figure 1 contains a schematic diagram of one example of a heater that can be used in the heating process in the present invention.

Figures 2 to 5 contain micrographs (3,000x) of the particle structures of the manganese oxide powders prepared in Examples 1 to 3 and Comparative Example 1, respectively.

1 : supersonic humidifier
2 : reaction tube
3 : electric furnace
4 : temperature controller
5 : collector
6 : water
7 : suction fan